Dipole autocorrelation function for molecular pressure broadening: A quantum theory which satisfies the fluctuation-dissipation theorem

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The dipole autocorrelation function for spectral line broadening is treated in a quantum theory which rigorously satisfies the fluctuation-dissipation theorem on a microscopic level. The basic approximation in the theory is the binary-collision approximation. In the present paper, the two-body interaction is decomposed into one part which commutes with the internal coordinates and another part which does not. The theory, as developed, is appropriate for broadening mechanisms for which the noncommuting term may be treated within the framework of perturbation theory, while the commuting term is to be treated exactly. The theory gives, at long times, a result for the dipole autocorrelation function consistent with the well-known impact approximation. At short times, an autocorrelation function of Gaussian form, with renormalization of the initial-state occupancy is obtained. It is found that the qualitative features discussed above are unaltered in higher-order perturbation theory. The results are consistent with the requirement that all time derivatives of the autocorrelation function at $t=0$ exist. This further satisfies the requirement that all moments of the line-shape function in the frequency domain exist, hence that the line-shape function decays "exponentially" sufficiently far in the wings.

I. INTRODUCTION

In the calculation of molecular pressure broadening, extensive use has been made of the autocorrelation function[1-3] for the dipole moment operator in the time domain. Using this method, the power spectrum for absorbed or emitted radiation is obtained from the Fourier transform of the autocorrelation function. This result follows from the quantum analog of the Wiener-Khintchine theorem[1] for classical correlation functions. In spite of the diverse formulations[4-14] which may be found in the literature, it appears that certain aspects of the theory remain incomplete or have not been adequately discussed.

If one is interested in details of the line shape over the full extent of the spectral transition, then it is not sufficient to consider times comparable to the time between collisions. Rather, in this case, one must also consider contributions to the autocorrelation function associated with times as small, or smaller, than the duration of collision. However, any rigorous treatment for small times must certainly satisfy the fluctuation-dissipation theorem (FDT).[1,15-18] The FDT (also known as detailed balance) has been incorporated into a number of essentially phenomenological theories,[19-21] using the Egelstaff-Schofield[22,23] complex-time transformation. These theories force the FDT to be valid on a line-by-line basis, using an autocorrelation function involving a number of adjustable parameters, typically a time between collisions τ_c and a quantity that may be associated with a duration of collision τ_d. To our knowledge, no microscopic formulation which satisfies the FDT has been presented in the literature. In this paper we provide such a formulation. The present theory will also provide an explicit microscopic description for the short-time behavior of the autocorrelation function, and for the transition to the long-time regime for which the impact approximation is generally considered to be valid. These two aspects have remained unclear in most previous formulations.

In the present paper, the only essential approximation is the binary collision approximation. For problems involving atmospheric densities this appears to be justified from experimental observations of the density dependence of half widths and far-wing absorption.

Also, throughout most sections of this paper, for simplicity of notation and discussion, we shall neglect line-coupling[5-6,24-29] effects. However, in

Appendix B we present the general result within the binary-collision approximation which rigorously includes line-coupling contributions. Calculations based on this more general formalism will undoubtedly be difficult, but should be tractable.

In the present formulation we shall separate the interaction Hamiltonian into two parts. The rigorous distinction between these two parts is that one commutes with the internal coordinates of the molecules while the second does not. We shall thus refer to these as "commuting" and "noncommuting" interaction terms, respectively. In molecular pressure broadening these interactions have sometimes been denoted[11,30–33] as "isotropic" and "anisotropic"; however, these terms are unnecessarily restrictive and may lead to confusion. For example, in atomic spectral broadening one also may consider adiabatic,[34] electronic state-dependent (but angle-independent) interactions in which $V_{ii}(R)$ and $V_{ff}(R)$ may be significantly different. Similar interactions have been discussed for molecular spectra.[35,36] For the molecular case of primary concern in this paper, we follow a procedure of treating the commuting interactions exactly, while discussing the noncommuting interactions in perturbation theory. For certain problems in atomic spectral broadening, there may be other preferred procedures for treating the noncommuting interactions.

Within the above approximations we shall show, at small times, that the autocorrelation function for each line is of Gaussian form. This implies that all time derivatives exist at $t=0$; hence all spectral moments[10,13,19] of the line-shape function must also exist. This further implies that the line-shape function decays in some "exponential" fashion sufficiently far in the wings. The transition to the long-time impact regime will also be examined.

Finally, we might also mention that there are clearly other ways of proceeding, which, if pursued carefully, should lead to a theory which satisfies the FTD. We refer, in particular, to the finite-temperature perturbation theory,[37] with associated graphical methods,[38–47] or the double-time Green's-function[48] technique. We have chosen an approach which, within the binary-collision approximation, dispenses with the many-body aspect in a particularly simple fashion. It would, no doubt, be clumsy to attempt to go beyond the binary-collision approximation using the present formalism.

II. GENERAL THEORY

We shall write the absorption coefficient (cm^{-1}) in the form[19]

$$\alpha(\omega)=\frac{4\pi^2\omega n_{\mathrm{rad}}}{3c}\chi''(\omega)\,, \tag{2.1}$$

$$\chi''(\omega)=\tanh\left[\frac{\beta\hbar\omega}{2}\right]\times\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}e^{-i\omega t}[\phi(t)+\phi(-t)] \tag{2.2a}$$

$$=(1-e^{-\beta\hbar\omega})\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}e^{-i\omega t}\phi(t) \tag{2.2b}$$

$$=\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}e^{-i\omega t}[\phi(t)-\phi(-t)]\,. \tag{2.2c}$$

In these equations, n_{rad} is the number density of radiating molecules, $\beta=(k_BT)^{-1}$, and $\phi(t)$ is the autocorrelation function given by

$$\phi(t)=\mathrm{Tr}[\rho(H)\vec{\mu}(0)\cdot\vec{\mu}(t)]\,, \tag{2.3a}$$

$$\phi(-t)=\mathrm{Tr}[\rho(H)\vec{\mu}(0)\cdot\vec{\mu}(-t)] \tag{2.3b}$$

$$=\mathrm{Tr}[\rho(H)\vec{\mu}(t)\cdot\vec{\mu}(0)]\,, \tag{2.3c}$$

where $\vec{\mu}(t)$ is the Heisenberg operator

$$\vec{\mu}(t)=\exp(iHt/\hbar)\vec{\mu}(0)\exp(-iHt/\hbar) \tag{2.4}$$

and

$$\rho(H)=e^{-\beta H}/\mathrm{Tr}(e^{-\beta H}) \tag{2.5a}$$

$$=e^{-\beta H}/Z \tag{2.5b}$$

is the canonical density matrix. The Hamiltonian H is for a system consisting of one radiating (absorbing) molecule and N_p perturbers with which it may interact.

The equivalence of formulas (2.2a)–(2.2c) is contained in the time-domain statement[19] of the FDT, i.e.,

$$\phi(-t)=\phi(t+i\beta\hbar)\,. \tag{2.6}$$

This result is readily proven from Eqs. (2.3a)–(2.3c) using cyclic invariance and the fact that $\exp[\pm(iHt/\hbar)]$ commute with $\rho(H)$; Eq. (2.6) must also be consistent with the relation

$$\phi(-t)=[\phi(t)]^*\,, \tag{2.7}$$

which guarantees that $\alpha(\omega)$ is real.

From Eqs. (2.3a)–(2.3c) we may write

$$\phi(t)=Z^{-1}\mathrm{Tr}\{\vec{\mu}\exp(iHt/\hbar)\cdot\vec{\mu}\exp[(-iH/\hbar)(t-i\beta\hbar)]\}\ , \tag{2.8a}$$

$$\phi(-t)=\phi(t+i\beta\hbar)$$
$$=Z^{-1}\mathrm{Tr}\{\exp[(iH/\hbar)(t+i\beta\hbar)]\vec{\mu}\cdot\exp(-iHt/\hbar)\vec{\mu}\}\ . \tag{2.8b}$$

In what follows it will be convenient to decompose the Hamiltonian H according to

$$H=H_0+V\ , \tag{2.9}$$

where H_0 contains the unperturbed energies of the molecules along with that part of the intermolecular interaction which commutes with the internal coordinates. Thus V is taken to contain the noncommuting perturbing forces. [See the discussion following Eq. (3.3) of Sec. III where this breakup is explicitly utilized.]

Now in Eqs. (2.8a) and (2.8b) we introduce the time-development operator $U(t)$ defined by

$$\exp(-iHt/\hbar)=\exp(-iH_0t/\hbar)U(t)\ , \tag{2.10a}$$

$$\exp(iHt/\hbar)=U^{\dagger}(t)\exp(iH_0t/\hbar)\ , \tag{2.10b}$$

or, more generally, for complex time z,

$$\exp(-iHz/\hbar)=\exp(-iH_0z/\hbar)U(z) \tag{2.11a}$$

with adjoint relation

$$\exp(iHz^*/\hbar)=U^{\dagger}(z)\exp(iH_0z^*/\hbar)\ . \tag{2.11b}$$

From the above relations, one readily sees that $U(t)$ is unitary for real t. Making use of these definitions, we obtain

$$\phi(t)=\nu\,\mathrm{Tr}[\rho(H_0)U(t-i\beta\hbar)\vec{\mu}U^{\dagger}(t)\cdot\exp(iH_0t/\hbar)\vec{\mu}\exp(-iH_0t/\hbar)] \tag{2.12a}$$

and

$$\phi(-t)=\phi(t+i\beta\hbar)$$
$$=\nu\,\mathrm{Tr}[\rho(H_0)\exp(iH_0t/\hbar)\vec{\mu}\exp(-iH_0t/\hbar)U(t)\cdot\vec{\mu}U^{\dagger}(t-i\beta\hbar)]\ , \tag{2.12b}$$

where $\rho(H_0)=e^{-\beta H_0}/\mathrm{Tr}(e^{-\beta H_0})$ is the unperturbed density matrix, and where ν is the ratio

$$\nu\equiv\frac{Z_0}{Z}=\frac{\mathrm{Tr}(e^{-\beta H_0})}{\mathrm{Tr}(e^{-\beta H})}\ . \tag{2.13}$$

From Eq. (2.12b) it is clear, in a trivial fashion, that the FDT is still satisfied at this point. However, there are ways of rewriting all of these equations which make identifications far less obvious. For example, if we let $t\rightarrow -t$ in Eq. (2.12a), we obtain

$$\phi(-t)=\nu\,\mathrm{Tr}[\rho(H_0)U(-t-i\beta\hbar)\vec{\mu}U^{\dagger}(-t)\cdot\exp(-iH_0t/\hbar)\vec{\mu}\exp(iH_0t/\hbar)]\ . \tag{2.14}$$

The equivalence of Eqs. (2.12b) and (2.14) is now not trivial, and it must be obtained from various identities which we will presently derive. An even more subtle problem concerns the following point. One does not obtain a correct expression for $\phi(t+i\beta\hbar)$ by simply replacing t by $(t+i\beta\hbar)$ in the right-hand side of Eq. (2.12a). The reason is that in the $U^{\dagger}(t)$ operator of Eq. (2.12a), the two operations of complex-time translation $t\rightarrow t+i\beta\hbar$ and of taking the Hermitian adjoint do not commute. We shall show that the correct procedure is to eliminate the adjoint operation, and *then* to perform the complex-time translation.

The basic identity which we shall need is obtained as follows: in Eq. (2.11a) we replace z by $-z^*$ and obtain

$$\exp(iHz^*/\hbar)=\exp(iH_0z^*/\hbar)U(-z^*)\ . \tag{2.15}$$

We now equate Eqs. (2.11b) and (2.15) and obtain

$$U^{\dagger}(z)=\exp(iH_0z^*/\hbar)U(-z^*)$$
$$\times\exp(-iH_0z^*/\hbar)\ . \tag{2.16}$$

Some useful special cases for real t are

$$U^{\dagger}(t)=\exp(iH_0t/\hbar)U(-t) \times\exp(-iH_0t/\hbar)\ , \tag{2.17a}$$

$$U^{\dagger}(-t)=\exp(-iH_0t/\hbar)U(t) \times\exp(iH_0t/\hbar)\ , \tag{2.17b}$$

$$U(t)=\exp(iH_0t/\hbar)U^{\dagger}(-t)\exp(-iH_0t/\hbar)\ . \tag{2.17c}$$

The equivalence of Eqs. (2.12b) and (2.14) for $\phi(-t)$ can readily be established by starting from Eq. (2.12b), making use of Eq. (2.16) with $z=t-i\beta\hbar$, inserting Eq. (2.17c) for $U(t)$, and finally using cyclic invariance of the trace expression.

Next we return to the problem of correctly obtaining $\phi(t+i\beta\hbar)$ from $\phi(t)$. Starting from Eq. (2.12a), we make use of Eq. (2.17a) to eliminate the adjoint operation. This converts Eq. (2.12a) to read

$$\phi(t)=\nu\,\mathrm{Tr}[\rho(H_0)U(t-i\beta\hbar)\vec{\mu}\exp(iH_0t/\hbar)\cdot U(-t)\vec{\mu}\exp(-iH_0t/\hbar)]\ . \tag{2.18}$$

The complex time translation $t\rightarrow t+i\beta\hbar$ then gives

$$\phi(t+i\beta\hbar)=\nu\,\mathrm{Tr}\{\rho(H_0)U(t)\vec{\mu}\cdot\exp[iH_0(t+i\beta\hbar)/\hbar]U(-t-i\beta\hbar)\vec{\mu}\exp[-iH_0(t+i\beta\hbar)/\hbar]\}\ . \tag{2.19}$$

Now inserting Eq. (2.17c) for $U(t)$, Eq. (2.19) simplifies to give our previous expression (2.14) for

$$\phi(t+i\beta\hbar)=\phi(-t)\ .$$

We have discussed the above points in some detail because we will need to make use of similar manipulations to verify that the FDT is satisfied at later stages of the formulation. For later purposes, it will also prove convenient to introduce the integral equations for the $U(t)$ operators. With the boundary condition $U(0)=1$, one obtains the integral equations

$$U(t)=1-\frac{i}{\hbar}\int_0^t V(t')U(t')dt'\ , \tag{2.20a}$$

$$U^{\dagger}(t)=1+\frac{i}{\hbar}\int_0^t U^{\dagger}(t')V(t')dt' \tag{2.20b}$$

with

$$V(t)=\exp(iH_0t/\hbar)V\exp(-iH_0t/\hbar)\ . \tag{2.20c}$$

More generally, for complex t, we write

$$U(z)=1-\frac{i}{\hbar}\int_0^z V(z')U(z')dz' \tag{2.21a}$$

with

$$V(z')=\exp(iH_0z'/\hbar)V\exp(-iH_0z'/\hbar)\ , \tag{2.21b}$$

where the integration can be taken over any path in the complex z' plane where the integrand is analytic.

To conclude this section, it is interesting to compare Eq. (2.12a) for $\phi(t)$ with the result one obtains in an analogous theory which does not satisfy the FDT. In such a theory, which ignores so-called "back reaction," $\rho(H)$ is approximated by the unperturbed density $\rho(H_0)$ and leads to the result

$$\phi(t)\simeq\mathrm{Tr}[\rho(H_0)U(t)\vec{\mu}U^{\dagger}(t)\cdot\exp(iH_0t/\hbar)\vec{\mu}\exp(-iH_0t/\hbar)]\ . \tag{2.22}$$

Comparison of Eqs. (2.12a) and (2.22) shows that in the more complete theory, $U(t)$ is replaced by $U(t-i\beta\hbar)$ and a normalization factor $\nu=Z_0/Z$ is introduced.

III. BINARY-COLLISION AND UNCOUPLED-LINE APPROXIMATIONS

In this section, we shall assume low or atmospheric densities, and hence we make the binary-collision approximation. For clarity and ease of presentation we shall also ignore line-coupling contributions. The complete generalization of the theory to include line-coupling effects is presented in Appendix B. To facilitate these approximations, it is convenient to separate out the internal states of the radiating molecule in the expression for H_0. Thus we write

$$H_0=H_{RI}^0+\tilde{H}_0\ , \tag{3.1}$$

where H_{RI}^0 contains only the internal coordinates of

the radiating molecule. Then $\tilde{H}_0$ contains all the rest of the unperturbed Hamiltonian, i.e., the internal coordinates of all perturbers, the translational coordinates of all molecules (including the radiator), and the commuting interactions between the radiator and perturbers. The unperturbed density matrix then factors as

$$\rho(H_0)=\rho(H_{RI}^0)\rho(\tilde{H}_0) .$$

The operator $\rho(\tilde{H}_0)$ can also be further factored; however, it is convenient not to use this at present.

We denote the eigenstates of H_{RI}^0 by $|jm\rangle$, where m is the magnetic quantum number and where j stands for all other quantum numbers necessary to specify the internal state. Now in Eq. (2.12a) we take the trace over $\rho(H_{RI}^0)$ and find

$$\phi(t)=\nu \sum_{j_i,j_i',j_f,j_f'} \sum_{m_i,m_i',m_f,m_f'} \rho(\epsilon_{j_i'})\exp[(i/\hbar)(\epsilon_{j_f'}-\epsilon_{j_i'})t]\langle j_i m_i \mid \vec{\mu} \mid j_f m_f\rangle \cdot \langle j_f' m_f' \mid \vec{\mu} \mid j_i' m_i'\rangle$$
$$\times \mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i' m_i' \mid U(t-i\beta\hbar) \mid j_i m_i\rangle\langle j_f m_f \mid U^\dagger(t) \mid j_f' m_f'\rangle] , \tag{3.2}$$

with

$$\rho(\epsilon_{j_i'})=e^{-\beta\epsilon_{j_i'}} \Big/ \sum_j (2j+1)e^{-\beta\epsilon_j} . \tag{3.3}$$

In obtaining the above result from Eq. (2.12a), we have used the fact that

$$\exp(iH_0 t/\hbar)\vec{\mu}\exp(-iH_0 t/\hbar)=\exp(iH_{RI}^0 t/\hbar)\vec{\mu}\exp(-iH_{RI}^0 t/\hbar) ,$$

because the remainder of the unperturbed Hamiltonian ($\tilde{H}_0$) commutes with the internal coordinates of the radiator, and hence also with $\vec{\mu}$. Comparison of Eq. (3.2) with the analogous result derived from Eq. (2.22) which does not satisfy the FDT,

$$\phi(t)= \sum_{j_i,j_i',j_f,j_f'} \sum_{m_i,m_i',m_f,m_f'} \rho(\epsilon_{j_i'})\exp[(i/\hbar)(\epsilon_{j_f'}-\epsilon_{j_i'})t]\langle j_i m_i \mid \vec{\mu} \mid j_f m_f\rangle \cdot \langle j_f' m_f' \mid \vec{\mu} \mid j_i' m_i'\rangle$$
$$\times \mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i' m_i' \mid U(t) \mid j_i m_i\rangle\langle j_f m_f \mid U^\dagger(t) \mid j_f' m_f'\rangle] , \tag{3.4}$$

again exhibits two differences: (a) The factor of $\nu=Z_0/Z$ in Eq. (3.2) and (b) $U(t)\leftrightarrow U(t-i\beta\hbar)$.

At this point, we shall make the uncoupled-line approximation, $j_f'=j_f$ and $j_i'=j_i$. This is really not necessary and is done largely for simplicity of discussion. The reader is referred to Appendix B for the generalization to include line coupling. Additionally, in a separate publication one of the present authors (R.W.D.) will present a somewhat simplified approach which is meant to be applicable only in the far wings. This T-matrix formulation is carried out in the frequency domain, it satisfies the FDT, and it correctly includes all possible line-coupling effects.

If we now apply the uncoupled-line approximation to Eq. (3.2) and then make use of the Wigner-Eckhart theorem for the $\vec{\mu}$ matrix elements, we obtain

$$\phi(t)=\nu \sum_{j_i,j_f} \rho(\epsilon_{j_i})(2_{j_i}+1)\,|\langle j_i||\mu||j_f\rangle|^2$$
$$\times C_{\mathrm{if}}(t)\exp[(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})t] , \tag{3.5}$$

where the reduced matrix elements satisfy the symmetry relation

$$(2_{j_f}+1)\,|\langle j_f||\mu||j_i\rangle|^2 = (2j_i+1)\,|\langle j_i||\mu||j_f\rangle|^2 \tag{3.6}$$

and where $C_{\mathrm{if}}(t)$ is a correlation function given by

$$C_{\mathrm{if}}(t)=\frac{1}{(2j_i+1)} \sum_{m_i,m_i',m_f,m_f',m} (j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f 1 m_f' m \mid j_f 1 j_i m_i')$$
$$\times \mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i m_i' \mid U(t-i\beta\hbar) \mid j_i m_i\rangle\langle j_f m_f \mid U^\dagger(t) \mid j_f m_f'\rangle] . \tag{3.7}$$

Before proceeding to make the binary-collision approximation, it is interesting to note the normalization

properties of Eqs. (3.5) and (3.7). First we note that $C_{if}(0)\neq 1$. Rather, from Eq. (3.7), we obtain

$$C_{if}(0)=\frac{1}{(2j_i+1)}\sum_{m_i,m_i'}\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i m_i' \mid U(-i\beta\hbar)\mid j_i m_i\rangle] \times\sum_{m_f,m}(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f 1 m_f m \mid j_f 1 j_i m_i') \ . \tag{3.8}$$

Performing the sum over m_f,m in Eq. (3.8) simply produces a factor of $\delta_{m_i,m_i'}$, and leads to

$$C_{if}(0)=C_i(0)=\frac{1}{2j_i+1}\sum_{m_i}\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i m_i \mid U(-i\beta\hbar)\mid j_i m_i\rangle] \ . \tag{3.9}$$

Although this does not equal unity, we can write

$$C_{if}(t)=C_i(0)\tilde{C}_{if}(t) \tag{3.10}$$

or

$$\tilde{C}_{if}(t)=\frac{C_{if}(t)}{C_i(0)} \ ; \tag{3.11}$$

then $\tilde{C}_{if}(0)=1$, and we can rewrite Eq. (3.5) as

$$\phi(t)=\sum_{j_i,j_f}\tilde{\rho}(\epsilon_{j_i})\mid\langle j_i\mid\mid\mu\mid\mid j_f\rangle\mid^2\exp[(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})t]\tilde{C}_{if}(t) \ , \tag{3.12}$$

where

$$\tilde{\rho}(\epsilon_{j_i})\equiv\nu\rho(\epsilon_{j_i})(2j_i+1)C_i(0) \ . \tag{3.13}$$

We now show that $\tilde{\rho}(\epsilon_{j_i})$ is simply a *renormalized* initial-state occupancy and, in particular, that

$$\sum_{j_i}\tilde{\rho}(\epsilon_{j_i})=1 \ . \tag{3.14}$$

To prove this, we combine Eqs. (3.9), (3.13), and (3.14) to give

$$\sum_{j_i}\tilde{\rho}(\epsilon_{j_i})=\nu\sum_{j_i,m_i}\rho(\epsilon_{j_i})\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i m_i \mid U(-i\beta\hbar)\mid j_i m_i\rangle] =\nu\,\mathrm{Tr}[\rho(H_0)U(-i\beta\hbar)] \ , \tag{3.15}$$

where the trace is now over the *complete* unperturbed density matrix. However, it may readily be established that

$$\mathrm{Tr}[\rho(H_0)U(-i\beta\hbar)]=\frac{Z}{Z_0}=\nu^{-1} \tag{3.16}$$

from which the result (3.14) immediately follows.

Now the binary-collision approximation to Eq. (3.7) is simply

$$C_{if}(t)=[q_{if}(t)]^{N_P} \ , \tag{3.17}$$

where N_P is the number of perturbers and

$$q_{if}(t)=\frac{1}{(2j_i+1)}\sum_{m_i,m_i',m_f,m_f',m}(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f 1 m_f' m \mid j_f 1 j_i m_i') \times\mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_i m_i' \mid U_S(t-i\beta\hbar)\mid j_i m_i\rangle\langle j_f m_f \mid U_S^{\dagger}(t)\mid j_f m_f'\rangle] \ . \tag{3.18}$$

In the expression (3.18), the subscript S on the ρ and U operators denotes that these operators now correspond to a *single* radiator and perturber.

One next invokes the same argument used by Baranger[5] and others.[34,49] Namely, one assumes that $q_{if}(t)$ has the form

$$q_{if}(t)=\left[1+\frac{1}{\Omega}F_{if}(t)\right] \tag{3.19a}$$

$$=\left[1+\frac{n_P}{N_P}F_{if}(t)\right], \tag{3.19b}$$

where Ω is the normalization volume and n_p is the perturber density. Then in the limit of large N_P, Eqs. (3.17) and (3.19) yield

$$C_{if}(t)=\exp[n_P F_{if}(t)] \tag{3.20a}$$

or

$$C_{if}(t)=\exp\{N_P[q_{if}(t)-1]\} . \tag{3.20b}$$

In order to justify the form in Eqs. (3.19), we can begin by noting from analogy with Eqs. (2.20) and (2.21) that the U_S operators in Eq. (3.18) can be written in the form

$$U_S^\dagger(t)=1+W_S^\dagger(t) , \tag{3.21a}$$

$$U_S(t-i\beta\hbar)=1+W_S(t-i\beta\hbar) , \tag{3.21b}$$

where

$$W_S(t)=-\frac{i}{\hbar}\int_0^t V_S(t')U_S(t')dt' , \tag{3.22a}$$

$$W_S^\dagger(t)=\frac{i}{\hbar}\int_0^t U_S^\dagger(t')V_S(t')dt' , \tag{3.22b}$$

$$W_S(t-i\beta\hbar)=-\frac{i}{\hbar}\int_0^{t-i\beta\hbar} V_S(z')U_S(z')dz' . \tag{3.22c}$$

Then in Eq. (3.18), the term in the product of the U's, which is independent of time, may readily be shown to sum to unity which justifies the first term in Eq. (3.19a). The volume dependence of the second term in Eq. (3.19a) will be established at a later stage.

It is important, after having made the uncoupled-line and binary-collision approximations, to be able to demonstrate that the FDT is still rigorously satisfied. The proof that this is, indeed, the case is given in Appendix A. Briefly, the proof consists of first showing that the FDT is satisfied provided

$$C_{fi}(-t)=C_{if}(t+i\beta\hbar) \tag{3.23}$$

(note the exchange of indices i and f). In our binary-collision approximation (3.20b), the condition (3.23) is clearly satisfied provided we can show

$$q_{fi}(-t)=q_{if}(t+i\beta\hbar) . \tag{3.24}$$

The details of this proof are carried out in Appendix A. We also remark that in the uncoupled-line and binary-collision approximations, the reality condition, Eq. (2.7), is satisfied provided

$$C_{if}^*(t)=C_{if}(-t) ,$$

i.e., if

$$q_{if}^*(t)=q_{if}(-t) .$$

This relation can be proven using manipulations similar to those found in Appendix A.

Returning to Eq. (3.18) we can make use of Eqs. (3.22) to write

$$[q_{if}(t)-1]=\frac{1}{(2j_i+1)}\sum_{m_i,m_i',m_f,m_f',m}(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f 1 m_f' m \mid j_f 1 j_i m_i')$$
$$\times\{\mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_i m_i' \mid W_S(t-i\beta\hbar)\mid j_i m_i\rangle]\delta_{m_f',m_f}$$
$$+\mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_f m_f \mid W_S^\dagger(t)\mid j_f m_f'\rangle]\delta_{m_i',m_i}$$
$$+\mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_i m_i' \mid W_S(t-i\beta\hbar)\mid j_i m_i\rangle\langle j_f m_f \mid W_S^\dagger(t)\mid j_f m_f'\rangle]\} . \tag{3.25}$$

Once again, we can compare this to the result one obtains from Eqs. (2.22) and (3.4) which do not satisfy the FDT. In the simpler theory, $W_S(t-i\beta\hbar)$ is replaced by $W_S(t)$ in the first and third terms of Eqs. (3.25).

We also remark that the first two terms in Eq. (3.25) correspond to $[S(b)]_{\text{outer}}$ in Anderson theory,[3,50] while the last term corresponds to Anderson's $[S(b)]_{\text{inner}}$. In graphical perturbation theory[38–47] the two types of terms correspond to self-energy and vertex corrections, respectively.

IV. INVESTIGATION OF TIME DEPENDENCE IN LOW-ORDER PERTURBATION THEORY

In this section we shall discuss the long- and short-time behavior of the autocorrelation function within the context of perturbation theory, specifically up to second order in the noncommuting interactions. One can, of course, extend these procedures to higher order; however, for detailed calculations the Clebsch-Gordan algebra rapidly becomes difficult.

It is important, in the present context, to demand that the commuting part of the intermolecular potential be treated essentially exactly. This potential, which might be taken as a Lennard-Jones or Morse interaction, will contain a hard-core repulsive part which cannot, in general, be treated using perturbative procedures. This repulsive potential, in addition to providing the correct collision kinematics (e.g., curved versus straight-line trajectories) also prevents singularities from occurring in a perturbative treatment. It should be stressed, however, that this statement does not imply that the perturbative treatment necessarily converges. Although the use of realistic collision trajectories (through the inclusion of the isotropic potential) may be expected to improve convergence, it does not assure convergence. Thus, it may still be necessary in certain cases to employ some procedure to eliminate unphysical contributions, i.e., a procedure analogous to the Anderson-type cutoff.

We also remark that we have studied the time dependence of the present theory in higher-order perturbation theory, and we find the qualitative features (particularly the very short- and long-time behavior) to be unaltered. In addition, it appears that the FDT is satisfied order by order in perturbation theory, and hence the validity of this important result is not compromised by the perturbative technique.

In this section, in order to provide a more simplified account, we shall treat the internal states of both the radiator and perturber as nondegenerate, i.e., we shall ignore the $(2j+1)$-fold degeneracy in the m indices. This also means that we shall suppress the Clebsch-Gordan coefficients and the m summations in Eqs. (3.18) and (3.25) and shall set factors of $(2j+1)$ equal to unity. These details can easily be retained, but are important only for numerical calculations, which will not be attempted in this paper. As a final simplification in notation, we shall also drop the subscripts S on the ρ_s, U_S, W_S, and V_S operators which appear in Eqs. (3.18)–(3.25), understanding that these operators now refer to a single radiator and perturber.

We shall begin by considering the second term in Eq. (3.25), which we now simplify to read

$$K_f(t)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_f \mid W^{\dagger}(t) \mid j_f\rangle] . \tag{4.1}$$

This term enters in an identical fashion in both the theory which satisfies the FDT, and the one which does not. However, before considering this term in detail, we briefly remark on the other two terms of Eq. (3.25), which we also simplify as

$$K_i(t)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i \mid W(t-i\beta\hbar) \mid j_i\rangle] , \tag{4.2}$$

$$K_{\text{if}}(t)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i \mid W(t-i\beta\hbar) \mid j_i\rangle \times\langle j_f \mid W^{\dagger}(t) \mid j_f\rangle] . \tag{4.3}$$

Concerning Eq. (4.2), at large times ($|t| \gg \beta\hbar$) this term can be approximated by

$$K_i(t)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i \mid W(t) \mid j_i\rangle] \tag{4.4}$$

and the discussion in this regime is essentially identical to that which we present for $K_f(t)$ at large t. At very small times, $K_i(t)$ approaches the finite constant

$$K_i(0)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i \mid W(-i\beta\hbar) \mid j_i\rangle] \tag{4.5}$$

and, as discussed in Sec. III, leads to a renormalization of the initial-state occupancy. The discussion of Eq. (4.3) is somewhat more complicated and will be given separately.

In order to perform the trace in Eq. (4.1) we need the resolution of the identity operator in terms of the product states of H_0. This can be written

$$\sum_{j_f', J', \vec{k}'} |j_f' J' \psi_{\vec{k}'}\rangle\langle j_f' J' \psi_{\vec{k}'}| = 1 \tag{4.6}$$

with

$$|j_f' J' \psi_{\vec{k}'}\rangle = |j_f'\rangle |J'\rangle |\psi_{\vec{k}'}\rangle , \tag{4.7}$$

where $|j_f'\rangle$ denotes an internal state of the radiator, $|J'\rangle$ denotes an internal state of the perturber, and $|\psi_{\vec{k}'}\rangle$ is an eigenstate of the Hamiltonian

$$H^0_{IS0}=-\frac{\hbar^2\nabla^2}{2m}+V_0(r)\ . \tag{4.8}$$

In Eq. (4.8), $\nabla^2=\nabla^2_{\vec{r}}$, with $\vec{r}=\vec{r}_1-\vec{r}_2$, the relative coordinate;

$$m=m_1m_2/(m_1+m_2)\ ,$$

the reduced mass; and $V_0(r)$ is the commuting pair potential. Since $\vec{\mu}$, V_0, and V do not depend on the center-of-mass coordinate $\vec{R}$ of the pair, it can be seen that the translational motion of the center of mass plays no role in the subsequent theory. We thus have

$$\left[-\frac{\hbar^2\nabla^2}{2m}+V_0(r)\right]|\psi_{\vec{k}}\rangle=\epsilon_{\vec{k}}|\psi_{\vec{k}}\rangle\ . \tag{4.9}$$

For unbound states $|\psi_{\vec{k}}\rangle$ can be taken as any suitably normalized set of continuum eigenstates, and $\epsilon_{\vec{k}}=\hbar^2k^2/2m$. However, if $V_0(r)$ leads to bound states, sums over $|\psi_{\vec{k}}\rangle$ implicitly contain a sum over the bound states. The unperturbed energy associated with a state $|j_fJ\psi_{\vec{k}}\rangle$ can then be written

$$\epsilon_{j_fJ\vec{k}}=\epsilon_{j_f}+\epsilon_J+\epsilon_{\vec{k}}\ . \tag{4.10}$$

If we now evaluate Eq. (4.1) in first-order perturbation theory using Eq. (3.22b), we obtain

$$K_f^{(1)}(t)=\frac{it}{\hbar}\sum_{J,\vec{k}}\rho(\epsilon_J)\rho(\epsilon_{\vec{k}})\langle j_fJ\psi_{\vec{k}}|V|j_fJ\psi_{\vec{k}}\rangle \tag{4.11}$$

with

$$\rho(\epsilon_{\vec{k}})\equiv e^{-\beta\epsilon_{\vec{k}}}\Big/\sum_{\vec{k}''}e^{-\beta\epsilon_{\vec{k}''}}\ . \tag{4.12}$$

The expression (4.11) is seen to be a linear function of t without any approximations. We note, however, that $K_f^{(1)}(t)$ is pure imaginary and it therefore contributes a phase shift, rather than damping, to the autocorrelation function $C_{if}(t)$. It can also be shown, for multipole interactions, that $K_f^{(1)}(t)$ vanishes when a sum over magnetic quantum numbers is performed[47] (which is suppressed here). In what follows, we shall therefore neglect these first-order phase shifts.

We next evaluate $K_f(t)$ in second-order perturbation theory and find

$$K_f^{(2)}(t)=-\frac{1}{\hbar^2}\sum_{J,\vec{k}}\rho(\epsilon_J)\rho(\epsilon_{\vec{k}})\sum_{j_f',J',\vec{k}'}|\langle\alpha|V|\beta\rangle|^2f(t)\ , \tag{4.13}$$

where, for simplicity, $|\alpha\rangle\equiv|j_fJ\psi_{\vec{k}}\rangle$, $|\beta\rangle\equiv|j_f'J'\psi_{\vec{k}'}\rangle$, and

$$f(t)=-\frac{i\hbar}{\epsilon_\alpha-\epsilon_\beta}\left[t-i\hbar\frac{\exp[-(i/\hbar)(\epsilon_\alpha-\epsilon_\beta)t]-1}{\epsilon_\alpha-\epsilon_\beta}\right]\ . \tag{4.14}$$

An alternative and useful form for the $f(t)$ function is

$$f(t)=\frac{1}{\omega_{\alpha\beta}^2}[1-\cos(\omega_{\alpha\beta}t)]-\frac{i}{\omega_{\alpha\beta}^2}[\omega_{\alpha\beta}t-\sin(\omega_{\alpha\beta}t)]\ , \tag{4.15}$$

where $\omega_{\alpha\beta}\equiv(\epsilon_\alpha-\epsilon_\beta)/\hbar$. In this second form it is immediately clear that the real part of $f(t)$ is an even function of t, while the imaginary part is odd. Also, from Eqs. (4.13) and (4.15), we see that the real part of $K_f^{(2)}(t)$ is always negative (gives damping).

The time dependence of $K_f^{(2)}(t)$ for long and short times can now be deduced from a study of the $f(t)$ function. First we note that $f(t)$ is a perfectly well-behaved function when $(\epsilon_\alpha-\epsilon_\beta)\to0$. By expanding the exponential in Eq. (4.14), we find

$$f(t)\simeq\tfrac{1}{2}t^2\ , \tag{4.16}$$

as

$$(\epsilon_\alpha-\epsilon_\beta)\to0\ .$$

Furthermore it is clear that the above result is precisely what we get in the small-time limit $t\to0$. Hence, for short times,

$$K_f^{(2)}(t)\simeq-\frac{t^2}{2\hbar^2}\sum_{J,\vec{k}}\rho(\epsilon_J)\rho(\epsilon_{\vec{k}})\sum_{j_f',J',\vec{k}'}|\langle j_fJ\psi_{\vec{k}}|V|j_f'J'\psi_{\vec{k}'}\rangle|^2\ . \tag{4.17}$$

Thus, as $t\to0$, $K^{(2)}(t)$ is a real, quadratic function of time and from Eq. (3.20b) it leads to a correlation function of *Gaussian* form.

In order to examine the long-time behavior, we make use of the identities[51]

$$\lim_{|t|\to\infty}\frac{[1-\cos(\omega_{\alpha\beta}t)]}{\omega_{\alpha\beta}^2}=\pi\delta(\omega_{\alpha\beta})\,|t|\ , \tag{4.18}$$

$$\lim_{|t|\to\infty}\frac{1}{\omega_{\alpha\beta}^2}[\omega_{\alpha\beta}t-\sin(\omega_{\alpha\beta}t)]=t\mathscr{P}\frac{1}{\omega_{\alpha\beta}}\ . \tag{4.19}$$

Hence the long-time limit of $K_f^{(2)}(t)$ is given by

$$K_f^{(2)}(t)=-\frac{|t|}{\hbar}\sum_{J,\vec{k}}\sum_{j_f',J',\vec{k}'}\rho(\epsilon_J)\rho(\epsilon_{\vec{k}})\,|\langle j_fJ\psi_{\vec{k}}\,|\,V\,|\,j_f'J'\psi_{\vec{k}'}\rangle|^2\pi\delta(\epsilon_{j_fJ\vec{k}}-\epsilon_{j_f'J'\vec{k}'})$$
$$-\frac{it}{\hbar}\sum_{J,\vec{k}}\sum_{j_f'J',\vec{k}'}\rho(\epsilon_J)\rho(\epsilon_{\vec{k}})\,|\langle j_fJ\psi_{\vec{k}}\,|\,V\,|\,j_f'J'\psi_{\vec{k}'}\rangle|^2\mathscr{P}\frac{1}{(\epsilon_{j_fJ\vec{k}}-\epsilon_{j_f'J'\vec{k}'})}\ . \tag{4.20}$$

The above result is identical to the impact approximation[47,52] in second-order perturbation theory. The appearance of $|t|$ in the damping term is also familiar in the impact theory. If one assumes Eq. (4.20) to be valid for all times, including the neighborhood of $t=0$, the factor $|t|$ leads to singularities in the derivatives of $C_{if}(t)$ at $t=0$. This immediately implies that the higher-order moments[19] of the line-shape function [the Fourier transform of $C_{if}(t)$] do not exist in the impact theory. As we have seen from Eq. (4.17), the correct damping of $C_{if}(t)$ at small t is Gaussian, which implies that all moments of the line-shape function are well defined and finite. In the frequency domain, these results imply that the extreme far wings must decay in some exponential fashion, rather than the simple $(\omega-\omega_{fi})^{-2}$ decay predicted by the impact theory.

For intermediate times, it is clear that the time dependence of $K_f^{(2)}(t)$ is complicated, and it will probably need to be extracted numerically. A rough criterion for the intermediate-time region is $\langle\omega_{\alpha\beta}\rangle t\simeq 1$, where $\langle\omega_{\alpha\beta}\rangle$ is some average energy difference. For a situation in which $\hbar\langle\omega_{\alpha\beta}\rangle\simeq k_BT$, we estimate the transition region to occur at times of order

$$t\simeq\hbar/k_BT=\beta\hbar=2.6\times10^{-14}\ \text{sec}\ ,$$

for $T=296$ K. It is then clear that this is precisely the range where the difference between $W(t-i\beta\hbar)$ and $W(t)$ begins to be important in the $K_i(t)$ term.

Before going on, we remark that the long-time behavior of the term $K_i^{(2)}(t)$ [with $W(t-i\beta\hbar)\simeq W(t)$] can be obtained from Eq. (4.20) with the substitutions $j_f\to j_i$, $j_f'\to j_i'$, and with the imaginary term in Eq. (4.20) changing sign. This implies that the real parts of $K_i^{(2)}(t)$ and $K_f^{(2)}(t)$ add while the imaginary parts subtract. This is also familiar from the impact theory.

A second item that can be disposed of at this point is justification of the normalization volume dependence in the second term of Eq. (3.19a), i.e., we now show that $K_f^{(2)}(t)$, as given by Eqs. (4.17) and (4.20), is correctly proportional to $1/\Omega$. To see this we rewrite Eq. (4.12) as

$$\rho(\epsilon_{\vec{k}})=\frac{1}{\Omega}e^{-\beta\epsilon_{\vec{k}}}\Big/\left[\frac{1}{\Omega}\sum_{\vec{k}''}e^{-\beta\epsilon_{\vec{k}''}}\right]\ . \tag{4.21}$$

In the limit of large Ω,

$$\frac{1}{\Omega}\sum_{\vec{k}''}\to\frac{1}{(2\pi)^3}\int d^3k''\ ,$$

and the remaining factor of $1/\Omega$ in Eq. (4.21) turns out to give the expected $1/\Omega$ volume dependence of $K_f^{(2)}(t)$. To complete the proof, we note that if $|\psi_{\vec{k}}\rangle$ is a continuum wave function, it will contain a normalization factor of $1/\sqrt{\Omega}$, while bound-state wave functions are normalized independent of Ω. Then in Eqs. (4.17) and (4.20), if $|\psi_{\vec{k}}\rangle$ and $|\psi_{\vec{k}'}\rangle$ are both continuum states, the square of the matrix element yields a factor of $1/\Omega^2$. This is just what is needed to turn the $\vec{k},\vec{k}'$ sums into integrals. Likewise, one sees that the volume dependence is correct for bound→free, and bound→bound matrix elements.

We next consider the more complicated quantity $K_{if}(t)$ as given by Eq. (4.3). It is also interesting to compare this with the quantity

$$\tilde{K}_{if}(t)=\mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i\,|\,W(t)\,|\,j_i\rangle\langle j_f\,|\,W^\dagger(t)\,|\,j_f\rangle]\ , \tag{4.22}$$

which obtains in the analogous theory where the FDT is not satisfied, and which differs from Eq. (4.3) in $t \leftrightarrow t - i\beta\hbar$ in the $W(t)$ operator. Regarding both Eqs. (4.3) and (4.22), we remark that if one confines the analysis to second-order perturbation theory, there are a number of interesting cases where K_{if} and $\tilde{K}_{if}$ vanish. This happens for linear and asymmetric rotor (radiating) molecules for the case of dipole-dipole or dipole-quadrupole interactions, because one obtains *diagonal* reduced matrix elements of the radiator's dipole moment operator. These results are also familiar from the Anderson theory,[3,50] i.e., $[S(b)]_{\text{inner}}$ makes no contribution in such cases.

We note from Eqs. (4.3) and (4.22) that $K_{if}(t)$ and $\tilde{K}_{if}(t)$ are already at least of second order in V. Then, to second order, evaluation of the formulas for large t gives

$$K_{if}^{(2)}(t) \simeq \tilde{K}_{if}^{(2)}(t) = \frac{2|t|}{\hbar} \sum_{J,\vec{k}} \sum_{J',\vec{k}'} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \langle j_i J \psi_{\vec{k}} | V | j_i J' \psi_{\vec{k}'} \rangle \langle j_f J' \psi_{\vec{k}'} | V | j_f J \psi_{\vec{k}} \rangle$$

$$\times \pi \delta(\epsilon_{J\vec{k}} - \epsilon_{J'\vec{k}'}) \, . \tag{4.23}$$

This is, again, the impact result, and $K_{if}^{(2)}(t)$ *subtracts* from the damping given by the $K_i^{(2)}(t)$ and $K_f^{(2)}(t)$ terms.

Next, for short times, Eq. (4.22) evaluates to give

$$\tilde{K}_{if}^{(2)}(t) \simeq \frac{t^2}{\hbar^2} \sum_{J,\vec{k}} \sum_{J',\vec{k}'} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \langle j_i J \psi_{\vec{k}} | V | j_i J' \psi_{\vec{k}'} \rangle \langle j_f J' \psi_{\vec{k}'} | V | j_f J \psi_{\vec{k}} \rangle \, . \tag{4.24}$$

This term is quadratic in time and subtracts from the damping given by $K_f^{(2)}(t)$. However, at very short times we should consider, instead of $\tilde{K}_{if}(t)$, the function $K_{if}(t)$ which satisfies the FDT. Its small-time limit is

$$K_{if}^{(2)}(t) = \frac{t^2}{2\hbar^2} \sum_{J,\vec{k}} \sum_{J',\vec{k}'} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \{\exp[\beta\hbar(\omega_{J\vec{k}} - \omega_{J'\vec{k}'})] + 1\} \langle j_i J \psi_{\vec{k}} | V | j_i J' \psi_{\vec{k}'} \rangle \langle j_f J' \psi_{\vec{k}'} | V | j_f J \psi_{\vec{k}} \rangle$$

$$- \frac{it}{\hbar^2} \sum_{J,\vec{k}} \sum_{J',\vec{k}'} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \frac{1}{\omega_{J\vec{k}} - \omega_{J'\vec{k}'}} \{\exp[\beta\hbar(\omega_{J\vec{k}} - \omega_{J'\vec{k}'})] - 1\}$$

$$\times \langle j_i J \psi_{\vec{k}} | V | j_i J' \psi_{\vec{k}'} \rangle \langle j_f J' \psi_{\vec{k}'} | V | j_f J \psi_{\vec{k}} \rangle \, . \tag{4.25}$$

We note, that although $K_{if}^{(2)}(t)$ contains a term linear in t, this term corresponds to a phase shift rather than damping. Hence, we again find that the damping occurs quadratically at small t. Finally, for completeness, we quote the general results for $K_{if}^{(2)}(t)$ and $K_i^{(2)}(t)$ in second-order perturbation theory:

$$K_{if}^{(2)}(t) = -\sum_{J,\vec{k}} \sum_{J',\vec{k}'} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \langle j_i J \psi_{\vec{k}} | V | j_i J' \psi_{\vec{k}'} \rangle \langle j_f J' \psi_{\vec{k}'} | V | j_f J \psi_{\vec{k}} \rangle \frac{\exp[(i/\hbar)(\epsilon_{J'\vec{k}'} - \epsilon_{J\vec{k}})t] - 1}{\epsilon_{J'\vec{k}'} - \epsilon_{J\vec{k}}}$$

$$\times \frac{\exp[(i/\hbar)(\epsilon_{J\vec{k}} - \epsilon_{J'\vec{k}'})(t - i\beta\hbar)] - 1}{\epsilon_{J\vec{k}} - \epsilon_{J'\vec{k}'}} \, . \tag{4.26}$$

The long-time ($|t| \gg \beta\hbar$) limit [Eq. (4.23)] is obtained from this formula by again using the identity (4.18). The short-time limit leads directly to Eq. (4.25). For $K_i^{(2)}(t)$, we find

$$K_i^{(2)}(t) = -\frac{1}{\hbar^2} \sum_{J,\vec{k}} \rho(\epsilon_J)\rho(\epsilon_{\vec{k}}) \sum_{j_i', J', \vec{k}'} |\langle j_i J \psi_{\vec{k}} | V | j_i' J' \psi_{\vec{k}'} \rangle|^2 \tilde{f}(t) \tag{4.27}$$

with

$$\tilde{f}(t) = \frac{i\hbar}{(\epsilon_\alpha - \epsilon_\beta)} \left[(t - i\beta\hbar) + i\hbar \frac{\exp[(i/\hbar)(\epsilon_\alpha - \epsilon_\beta)(t - i\beta\hbar)] - 1}{(\epsilon_\alpha - \epsilon_\beta)} \right] \tag{4.28}$$

and where $\epsilon_\alpha \equiv \epsilon_{j_i J \vec{k}}$ and $\epsilon_\beta \equiv \epsilon_{j_i' J' \vec{k}'}$. It is not difficult to show explicitly that our second-order result for $[q_{if}(t)-1]$, as obtained from Eqs. (4.13), (4.27), and (4.26), satisfies the FDT, and it appears that the FDT is satisfied order by order in perturbation theory.

We conclude this section with one strong word of caution, namely, that one *cannot* obtain the far-wing line shape by Fourier transformation of the small-time behavior as given, for example, by Eq. (4.17). To be more specific, we note from Eq. (4.17) that the small-time behavior of the autocorrelation function $C_{if}(t)$ is essentially Gaussian. If one Fourier transforms the Gaussian, the result is, of course, a Gaussian line-shape function. But this expression leads to a totally spurious dependence of the absorption coefficient on the perturber density. It is known from experiment, at low densities, that the absorption coefficient in the far wings is proportional to the product of the radiator and perturber densities. Furthermore, it is apparent where the correct dependence on the perturber density comes from; namely, it arises when the exponential in Eq. (3.20b) is well approximated by

$$C_{if}(t) \simeq 1 + N_p[q_{if}(t)-1] \; . \tag{4.29}$$

The first term above leads to a delta function at the line center, and the second term gives an approximation to the far-wing line shape which is linear in the perturber density. Although the above approximation has something to do with "small times," it is really more of an expansion in density rather than in time.

V. DISCUSSION

Within the binary-collision and uncoupled-line approximations, we have derived an expression for the dipole autocorrelation function which rigorously satisfies the fluctuation-dissipation theorem. We have shown how these results go into the impact theory at large times. For short times we have found that $C_{if}(t)$ is damped in a Gaussian fashion. Although our analysis in Sec. IV was confined to second-order perturbation theory for the noncommuting interaction, by going to third order, we can easily convince ourselves that the above behavior is completely general, and only the details are altered in higher-order perturbation theory. These results imply that the line-shape function in the frequency domain must decay in some exponential fashion sufficiently far in the wings.

Although we have refrained from labeling the present formulation as a "unified" theory, we believe that it qualifies as such. One reason that we have avoided the above label is that most authors of unified treatments are content to show that their formulation goes into the impact limit at large times, and for small times takes the form of the quasistatic or statistical theory.[53–55]

We have shown that the present theory, indeed, does reduce to the impact approximation at large times. However, it is clear that the small-time limit of the present formulation is not equivalent to the statistical theory.

It is convenient to recognize, from a theoretical viewpoint, three regions of a spectral line (equivalently, there are three characteristic times of interest): (a) the line center region $|\Delta\omega|\tau_c \lesssim 1$, where τ_c is the time between collisions (impact region), (b) the region near $|\Delta\omega|\tau_d \simeq 1$, where τ_d is the duration of collision, and (c) the region $|\hbar\,\Delta\omega|\beta \gtrsim 1$, where the requirements of the FTD are important. Although, at low densities, we expect the present formalism to have validity in all three regions, the very short-time behavior which we have explicitly discussed refers primarily to region (c), and this limit is clearly not equivalent to the usual quasistatic or statistical theory. Once again, however, we caution that one cannot obtain the far-wing line shape by simply Fourier transforming the small-time limit of the autocorrelation function.

Although our main discussion has not specifically included line-coupling contributions, it is known that this approach may be inadequate for certain situations. To our knowledge, most previous treatments of spectral broadening which have included line-coupling contributions have been formulated within the framework of the impact approximation, e.g., the work of Baranger,[5] Kolb and Griem,[6] Ben-Reuven,[28] Gordon,[24,25] Rosenkranz,[26] Lam,[29] and Smith.[27] In the pressure regime below 1 atm, a great deal of effort has focused on the spectrum of O_2 at 60 GHz. For this case, line-coupling effects are observed at pressures as low as 200 Torr.[26,27,29] Effects of line coupling on spectral bands have been reported for other molecules, but for pressure regimes greater than 1 atm for which case other assumptions of the present theory, e.g., the binary-collision approximation, may not be satisfied.

Within the impact approximation, the situation concerning the effect of line coupling on the wings seems clear; namely, the result is to narrow the band, thus decreasing the wing absorption. This results from a certain interference between the indivi-

dual lines which comprise the band, and is related to the phenomenon of motional narrowing.[56,57]

An extension of the present theory to include line coupling is presented in Appendix B. Calculations based on this generalization will be difficult, but should remain tractable.

We would also like to remark on the relevance of the present theory to experimental data. It is true that accurate measurements of far-wing line shapes are difficult and often ambiguous, however, some do exist and they are of considerable interest for communications applications. One example is the measurements of Benedict *et al.*[58,59] for CO_2 beyond the R-branch band head at 2380 cm^{-1}. These authors have determined that the far-wing absorption is indeed exponential, as required by the existence of all spectral moments.

A second example is the measurements of Burch[60] of the H_2O "continuum" absorption in the 1000 cm^{-1} and 2500 cm^{-1} "window" spectral regions. In the case of H_2O, other absorption mechanisms have been postulated; however, it is important to study far-wing absorption before interpreting the contribution of more complicated absorption processes.

An area where a generalization of our present method would appear to be useful is the problem of collision-induced[61,62] absorption. These spectra are known to be asymmetric, and the FTD plays an important role in the interpretation of the line shapes. Most previous treatments of this problem have included detailed balance only on a phenomenological level.

Although our formulation has been completely quantum mechanical, this does not appear to preclude the use of semiclassical methods. In particular, the eigenstates $|\psi_{\vec{k}}\rangle$ of the isotropic Hamiltonian (4.8) might be chosen to be time-independent WKB wave functions. We hope to explore this and other computational possibilities in a future publication.

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APPENDIX A: PROOF THAT THE FDT IS SATISFIED IN THE BINARY-COLLISION AND UNCOUPLED-LINE APPROXIMATIONS

The first step in the proof is to show, for an uncoupled-line approximation of the form Eq. (3.5), that a sufficient condition for the FDT to be satisfied is

$$C_{fi}(-t)=C_{if}(t+i\beta\hbar)\ . \tag{A1}$$

The above relation applies to any uncoupled-line approximation and is not limited to the binary-collision case.

Now, starting from Eq. (3.5), we have

$$\phi(-t)=\nu\sum_{j_i,j_f}\rho(\epsilon_{j_i})(2j_i+1)\,|\,\langle j_i||\mu||j_f\rangle\,|^2\exp[-(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})t]C_{if}(-t)\ . \tag{A2}$$

We next interchange names of the dummy variables $i\leftrightarrows f$, and make use of the symmetry relation (3.6) for the reduced matrix elements. This gives

$$\phi(-t)=\nu\sum_{j_i,j_f}\rho(\epsilon_{j_f})(2j_i+1)\,|\,\langle j_i||\mu||j_f\rangle\,|^2\exp[(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})t]C_{fi}(-t)\ . \tag{A3}$$

Retaining this result we next obtain, from Eq. (3.5), the result

$$\phi(t+i\beta\hbar)=\nu\sum_{j_i,j_f}\rho(\epsilon_{j_i})(2j_i+1)\,|\,\langle j_i||\mu||j_f\rangle\,|^2 \times\exp[(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})(t+i\beta\hbar)]C_{if}(t+i\beta\hbar)\ . \tag{A4}$$

From Eq. (3.3) we note that

$$\rho(\epsilon_{j_i})\exp[-\beta(\epsilon_{j_f}-\epsilon_{j_i})]=\rho(\epsilon_{j_f}) . \tag{A5}$$

This gives

$$\phi(t+i\beta\hbar)=\nu\sum_{j_i,j_f}\rho(\epsilon_{j_f})(2j_i+1)\,|\,\langle j_i||\mu||j_f\rangle\,|^2\exp[(i/\hbar)(\epsilon_{j_f}-\epsilon_{j_i})t]C_{\rm if}(t+i\beta\hbar). \tag{A6}$$

Comparing Eqs. (A3) and (A6) we see that a sufficient condition for the FDT theorem [Eq. (2.6)] to be satisfied is just Eq. (A1). It is then clear, in our binary-collision approximation (3.20b), that (A1) is satisfied, provided that we can show

$$q_{fi}(-t)=q_{\rm if}(t+i\beta\hbar) . \tag{A7}$$

To prove the above result, we start from Eq. (3.18) and construct $q_{fi}(-t)$. To carry this out, we let $t\to -t$, $j_i\leftrightarrows j_f$, and it is also convenient to make the following changes in the dummy m-summation indices:

$$m_f\to m_i' \ , \ m_f'\to m_i \ , \ m_i'\to m_f \ , \ m_i\to m_f' \ , \ m\to -m . \tag{A8}$$

This leads to the result

$$q_{fi}(-t)=\frac{1}{2j_f+1}\sum_{m_i,m_i',m_f,m_f',m}(j_i 1m_i'-m\,|\,j_i 1j_f m_f')(j_i 1m_i-m\,|\,j_i 1j_f m_f)$$
$$\times{\rm Tr}[\rho_S(\tilde{H}_0)\langle j_f m_f\,|\,U_S(-t-i\beta\hbar)\,|\,j_f m_f'\rangle\langle j_i m_i'\,|\,U_S^\dagger(-t)\,|\,j_i m_i\rangle] . \tag{A9}$$

We next make use of the symmetry properties[50,63] of Clebsch-Gordan coefficients to obtain the identity

$$(j_i 1m_i'-m\,|\,j_i 1j_f m_f')(j_i 1m_i-m\,|\,j_i 1j_f m_f)=\frac{(2j_f+1)}{(2j_i+1)}(j_f 1m_f m\,|\,j_f 1j_i m_i)(j_f 1m_f' m\,|\,j_f 1j_i m_i') . \tag{A10}$$

Upon inserting this result into Eq. (A9), we obtain

$$q_{fi}(-t)=\frac{1}{(2j_i+1)}\sum_{m_i,m_i',m_f,m_f',m}(j_f 1m_f m\,|\,j_f 1j_i m_i)(j_f 1m_f' m\,|\,j_f 1j_i m_i')$$
$$\times{\rm Tr}[\rho_S(\tilde{H}_0)\langle j_f m_f\,|\,U_S(-t-i\beta\hbar)\,|\,j_f m_f'\rangle\langle j_i m_i'\,|\,U_S^\dagger(-t)\,|\,j_i m_i\rangle] . \tag{A11}$$

Retaining this result, we now want to compute $q_{\rm if}(t+i\beta\hbar)$, starting from Eq. (3.18) for $q_{\rm if}(t)$. Recalling our discussion in Sec. II, we have to be careful in performing this exercise. In particular, we have to eliminate the adjoint operation in Eq. (3.18) before making the complex-time translation $t\to t+i\beta\hbar$. Thus, we make use of Eq. (2.17a) to write

$$\langle j_f m_f\,|\,U_S^\dagger(t)\,|\,j_f m_f'\rangle=\langle j_f m_f\,|\,\exp(iH_0 t/\hbar)U_S(-t)\exp(-iH_0 t/\hbar)\,|\,j_f m_f'\rangle$$
$$=\exp(i\tilde{H}_0 t/\hbar)\langle j_f m_f\,|\,U_S(-t)\,|\,j_f m_f'\rangle\exp(-i\tilde{H}_0 t/\hbar) . \tag{A12}$$

Now inserting (A12) into Eq. (3.18), and then letting $t\to t+i\beta\hbar$, we find

$$q_{\rm if}(t+i\beta\hbar)=\frac{1}{(2j_i+1)}\sum_{m_i,m_i',m_f,m_f',m}(j_f 1m_f m\,|\,j_f 1j_i m_i)(j_f 1m_f' m\,|\,j_f 1j_i m_i')$$
$$\times{\rm Tr}\{\rho_S(\tilde{H}_0)\langle j_i m_i'\,|\,U_S(t)\,|\,j_i m_i\rangle$$
$$\times\exp[(i\tilde{H}_0/\hbar)(t+i\beta\hbar)]\langle j_f m_f\,|\,U_S(-t-i\beta\hbar)\,|\,j_f m_f'\rangle$$
$$\times\exp[(-i\tilde{H}_0/\hbar)(t+i\beta\hbar)]\} . \tag{A13}$$

Application of cyclic invariance turns the trace in Eq. (A13) into

$$\mathrm{Tr}\{\exp(-i\tilde{H}_0 t/\hbar)\langle j_i m_i' \mid U_S(t) \mid j_i m_i\rangle \exp(i\tilde{H}_0 t/\hbar)\rho_S(\tilde{H}_0)\langle j_f m_f \mid U_S(-t-i\beta\hbar) \mid j_f m_f'\rangle\} \ . \tag{A14}$$

We then note that

$$\begin{aligned}\exp(-i\tilde{H}_0 t/\hbar)\langle j_i m_i' \mid U_S(t) \mid j_i m_i\rangle \exp(i\tilde{H}_0 t/\hbar) &= \langle j_i m_i' \mid \exp(-iH_0 t/\hbar) U_S(t) \exp(iH_0 t/\hbar) \mid j_i m_i\rangle \\ &= \langle j_i m_i' \mid U_S^{\dagger}(-t) \mid j_i m_i\rangle \ ,\end{aligned} \tag{A15}$$

where we have made use of Eq. (2.17b) in the last step. Inserting (A15) into (A14) yields a further transformed trace:

$$\begin{aligned}&\mathrm{Tr}[\langle j_i m_i' \mid U_S^{\dagger}(-t) \mid j_i m_i\rangle \rho_S(\tilde{H}_0)\langle j_f m_f \mid U_S(-t-i\beta\hbar) \mid j_f m_f'\rangle] \\ &\qquad = \mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_f m_f \mid U_S(-t-i\beta\hbar) \mid j_f m_f'\rangle\langle j_i m_i' \mid U_S^{\dagger}(-t) \mid j_i m_i\rangle] \ .\end{aligned} \tag{A16}$$

Upon inserting (A16) into (A13), we find

$$\begin{aligned}q_{\mathrm{if}}(t+i\beta\hbar) = \frac{1}{(2j_i+1)} \sum_{m_i,m_i',m_f,m_f',m} &(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f 1 m_f' m \mid j_f 1 j_i m_i') \\ &\times \mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_f m_f \mid U_S(-t-i\beta\hbar) \mid j_f m_f'\rangle \\ &\times \langle j_i m_i' \mid U_S^{\dagger}(-t) \mid j_i m_i\rangle] \ .\end{aligned} \tag{A17}$$

The above result is seen to be identical to Eq. (A11) for $q_{fi}(-t)$. This completes the proof.

APPENDIX B: GENERALIZATION TO INCLUDE LINE COUPLING WITHIN THE BINARY-COLLISION APPROXIMATION

We start from Eq. (3.2), and apply the Wigner-Eckhart (WE) theorem to the $\vec{\mu}$ matrix elements. We use symmetry properties[50,63] of the Clebsch-Gordan coefficients, and with the reduced matrix elements defined by the relation (WE theorem)

$$\begin{aligned}&\langle j_i m_i \mid \vec{\mu} \mid j_f m_f\rangle = \langle j_i \| \mu \| j_f\rangle \sum_{m=0,\pm 1} \hat{\epsilon}_m (j_f 1 m_f m \mid j_f 1 j_i m_i) \ ; \\ &\hat{\epsilon}_0 = \hat{z}, \ \hat{\epsilon}_{-1} = \frac{(\hat{x}+i\hat{y})}{2} \ , \ \hat{\epsilon}_{+1} = -\frac{(\hat{x}-i\hat{y})}{2} \ ,\end{aligned} \tag{B1}$$

we invoke the symmetry property of reduced matrix elements

$$\langle j_f' \| \mu \| j_i'\rangle = (-1)^{j_i'-j_f'} \left[\frac{2j_i'+1}{2j_f'+1}\right]^{1/2} \langle j_i' \| \mu \| j_f'\rangle^* \ . \tag{B2}$$

This produces the result

$$\begin{aligned}&\langle j_i m_i \mid \vec{\mu} \mid j_f m_f\rangle\langle j_f' m_f' \mid \vec{\mu} \mid j_i' m_i'\rangle \\ &\qquad = \langle j_i \| \mu \| j_f\rangle\langle j_i' \| \mu \| j_f'\rangle^* \sum_{m=0,\pm 1} (j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f' 1 m_f' m \mid j_f' 1 j_i' m_i') \ .\end{aligned} \tag{B3}$$

Inserting this relation into Eq. (3.2) yields

$$\phi(t) = \nu \sum_{j_i,j_i',j_f,j_f'} \rho(\epsilon_{j_i'})(2j_i'+1)\langle j_i \| \mu \| j_f\rangle\langle j_f' \| \mu \| j_f'\rangle^* \exp[(i/\hbar)(\epsilon_{j_f'}-\epsilon_{j_i'})t] C_{i'i;ff'}(t) \ , \tag{B4}$$

where the correlation function $C(t)$ is given by

$$C_{i'i;ff'}(t)=\frac{1}{(2j_i'+1)}\sum_{m=0,\pm1}\sum_{m_i,m_i',m_f,m_f'}(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f' 1 m_f' m \mid j_f' 1 j_i' m_i') \times \mathrm{Tr}[\rho(\tilde{H}_0)\langle j_i' m_i' \mid U(t-i\beta\hbar)\mid j_i m_i\rangle\langle j_f m_f \mid U^{\dagger}(t)\mid j_f' m_f'\rangle] . \tag{B5}$$

These results are still exact, and it is clear that they reduce precisely to Eqs. (3.5) and (3.7) in the uncoupled-line approximation (where one simply sets $j_i'=j_i$ and $j_f'=j_f$). Now one can follow exactly the same route taken in Eqs. (3.17) through (3.20b), and one finds that within the binary-collision approximation the correlation function $C(t)$ is given by

$$C_{i'i;ff'}(t)=\exp\{N_p[q_{i'i;ff'}(t)-1]\} , \tag{B6}$$

where N_p is the number of perturbers, and with

$$q_{i'i;ff'}(t)=\frac{1}{(2j_i'+1)}\sum_{m=0,\pm1}\sum_{m_i,m_i',m_f,m_f'}(j_f 1 m_f m \mid j_f 1 j_i m_i)(j_f' 1 m_j' m \mid j_f' 1 j_i' m_i') \times \mathrm{Tr}[\rho_S(\tilde{H}_0)\langle j_i' m_i' \mid U_S(t-i\beta\hbar)\mid j_i m_i\rangle\langle j_f m_f \mid U_S^{\dagger}(t)\mid j_f' m_f'\rangle] . \tag{B7}$$

In this last equation, the subscripts S on ρ and the U's denote that these operators now refer to a single radiator and perturber.

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